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Resonant Interaction of Low Energy Electrons with Intramolecular Vibrations in Solid C_{60}

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The energy-dependant cross sections of the impact-excited intramolecular vibrations in an epitaxial $C_{60}(111)$ film have been measured by High Resolution Electron Energy Loss Spectroscopy (HREELS). A Negative Ion Resonance (NIR) behaviour is evidenced by a dramatic cross-section enhancement at a primary energy of ~2.9 eV together with some fine structures on the high energy side. Through comparison with experimental results on the unoccupied states and on the electronic excitations of solid C_{60}, these NIR structures can be correlated to a temporary trapping of the probing electron in the LUMO+3-derived state in the framework of an 'electronic excitation associated' NIR process.

1. INTRODUCTION

The formation of a negative ion due to the temporary trapping of a probing electron with an appropriate kinetic energy in an unoccupied electronic state, is a well known phenomenon in the electron spectroscopy of molecules, both in their gaseous and physisorbed phases, but sometimes also in chemisorbed species [1,2]. In the simplest process, so-called *shape-resonance*, the incident electron is trapped by a molecular affinity level forming a N+1 electron negative-ion state. This trapping can also occur with a simultaneous electronic excitation of the molecule. In this latter case, the incoming electron is bound to an electronically excited host so that this process can be called an *'electronic excitation associated resonance'* or a *'core-excited resonance'*. The formation of such negative ion states can prolong the effective interaction time of the incident electrons with the molecules and therefore, it constitutes an additional channel for electron scattering as the trapped electron is re-emitted from the negative ion state. This shows up in a resonant enhancement of the scattering cross section, which can be detected by High Resolution Electron Energy Loss Spectroscopy (HREELS) at a given kinetic energy of the probing electron.

The first indication for Negative Ion Resonances (NIR) in C_{60} was given by the observation of strong electron attachment phenomena in its gas phase [3,4]. Recently, Hunt *et al.* [5] have carried out a preliminary work about resonances for physisorbed C_{60} thin films on graphite, where they pointed out the importance of investigating the interface interaction of C_{60} with the substrate. As a matter of fact, no detailed study of NIR has been reported for solid C_{60} so far. Although it is known that the vibrational spectrum and the electronic structure of solid C_{60} look very similar to the gas phase one, C_{60} is not a pure van der Waals solid. Indeed, bond charge interactions contribute to the intermolecular bonding [6], which might affect the electron attachment process observed in the gaseous phase. Moreover, we should emphasise that the NIR study of solid state C_{60} can provide direct information on the electron-phonon coupling, which might lead to a better understanding of the phonon-mediated pairing mechanism thought to be responsible for the superconductivity in the fulleride salts [7].

In this paper we report on NIR in a thick $C_{60}(111)$ epitaxial film evidenced by HREELS measurements. A sharp resonant enhancement at 2.9 eV is observed which is very close to the previously reported value of 3.0 eV [5]. Furthermore, the comparison to Inverse PhotoEmission Spectroscopy (IPES) and EELS results allows us to assign the

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observed NIR phenomenon to an 'electronic excitation associated' shape resonance.

2. EXPERIMENTAL

The High Resolution Electron Energy Loss Spectroscopy (HREELS) measurements have been performed on a thick epitaxial C_{60} film grown on a Au(110) single crystal [8,9]. The experiments were carried out on an ISA Riber spectrometer with an incidence angle of 60° with respect to the sample normal, for both the specular and the off-specular geometry measurements. The base pressure was $7x10^{-11}$ mbar.

The sample was prepared in a separate interconnected chamber equipped with a Low Energy Electron Diffractometer (LEED) and a quadrupole mass analyser. The base pressure was in the low 10^{-10} mbar range.

The clean Au(110) surface was prepared by sputtering and annealing cycles. 99%-pure C_{60} was sublimed from a Knudsen cell at 750 K onto the clean Au(110)(1x2) surface, kept at 600 K. During evaporation, the pressure in the preparation chamber never exceeded the 10^{-9} mbar range. Sharp hexagonal LEED diffraction patterns testified to the high crystalline quality of the grown C_{60}(111) film.

3. RESULTS AND DISCUSSION

Typical HREELS spectra of our C_{60}(111) film are shown in Fig. 1, both in specular (a) and off-specular (b) geometry. These spectra look very similar to those previously reported in the literature [8,10] and we refer the reader to reference [10] for a detailed discussion. Let us however recall that in the specular geometry, the HREELS spectrum measured on an ordered surface is dominated by loss structures resulting from a long-range-interaction dipole scattering process, whereas off-specular geometry spectra show losses induced essentially by a short-range-interaction impact scattering process. The main features observed in Fig. 1a correspond indeed to the excitation of the four dipole-active T_{1u} modes: the very strong peak at 66 meV contains the first two T_{1u} modes (65.2 and 71.4 meV [10]) and the other two appear at 147 and 178 meV. In the tail of the huge 66 meV peak, two Raman active modes give rise to the 94 meV peak. On the other hand, in the off-specular geometry, not only dipole-active modes but also Raman and optically inactive modes can be observed. This is shown on Fig. 1b where the T_{1u} dipole-active

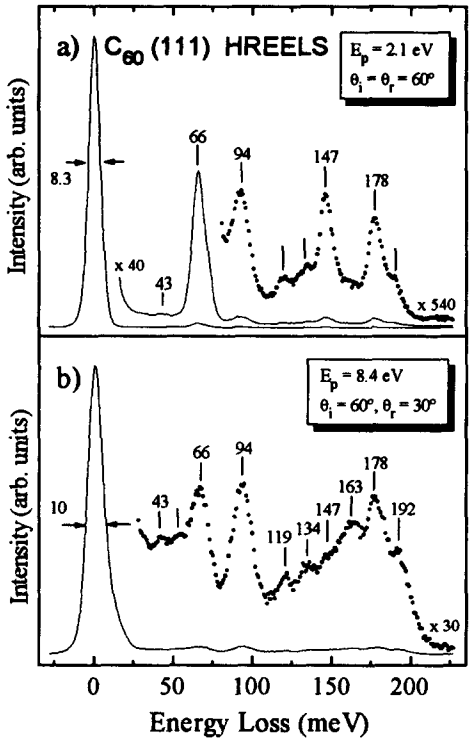

Figure 1: a) specular and b) off-specular geometry C_{60} (111) HREELS spectra with angles referred to the surface normal.

modes are still present but with a much reduced intensity, comparable to that of many other modes also observed by Raman [11] or Inelastic Neutron Scattering spectroscopies [12]. In fact, Non dipole-active modes were already detected in the specular geometry (43, 94, 119, 134 and 192 meV) but with a much weaker intensity relative to the dipole-active ones.

Since Negative Ion Resonance is a particular case of the impact scattering process, the best suited configuration to study this phenomenon by HREELS is the off-specular geometry [13].

Therefore we have recorded a set of off-specular geometry spectra for primary electron energies ranging from 1.8 eV to 7 eV. Fig. 2 illustrates clear changes in the relative intensities of the various vibrational excitations with varying primary energy. The present relative intensity evolution shows dramatic intensity variations which undoubtedly differ from what one would expect according to the basic HREELS theory [13]. In the present case, the relative intensities are strongly modulated for increasing primary energy : an obvious maximum intensity appears around E_p=3eV for the 155 and 192 meV excitations but clear indications for additional relative intensity modulations are also observed. For instance, the 134 meV peak reaches a maximum intensity around E_p=3.5eV where it becomes fully resolved. The big resonance around E_p=3eV reported by Hunt *et al.* [5] is thus not a single resonance but rather the main feature of a more complex resonant behaviour which we will try to inspect in more detail.

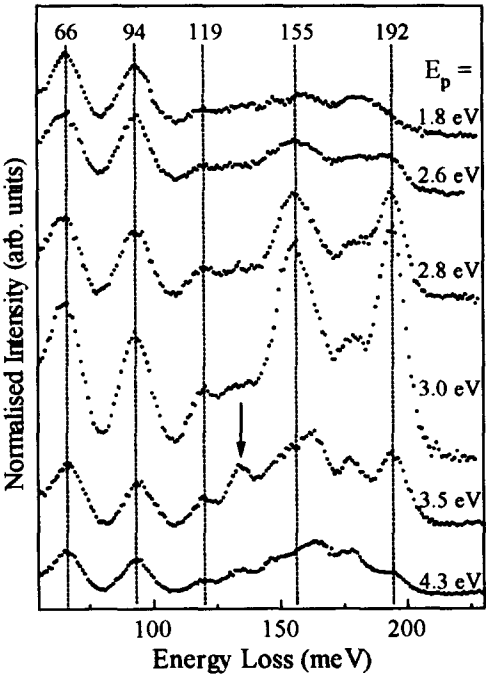

Figure 2: Evolution of the relative intensities with primary energy for off-specular geometry spectra normalised to the elastic peak.

To determine the relative intensity modulations more precisely, we have fitted each spectrum by a set of gaussian components that stand for all the peaks which are unambiguously observed in the spectra. It is then possible to plot the intensity evolution (with ~15% error bars) of each component with respect to the primary electron energy to get what we call a 'cross-section curve'. The cross-section curves do consequently not correspond to the intensity evolution of single C_{60} vibrational modes since most of the observed peaks result from the overlapping of several single vibrational modes [14,15].

The lower part of Fig. 3 displays the cross-section curves of the two peaks which show the largest resonant behaviour and give the clearest evidence for a Negative Ion Resonance. The main resonance appears around 2.9 eV and is confirmed as such by the coherent maximum observed in the intensity evolution of the first vibrational overtone (not shown here [16]). Besides the 2.9 eV feature, additional modulations in the cross-section curves clearly show up as a big asymmetry of the main feature and smaller structures for higher primary energies.

In the NIR process, the intermediate negative ion state closely resembles the final state of Inverse Photo-Emission Spectroscopy measurements which allow one to probe the empty electronic bands of a sample. Thus it should be useful to compare IPE spectra with the cross-section curves and hopefully find some correlation. Pedio *et al.* [17] have measured the IPES data displayed in Fig. 3 on the same C_{60}(111)/Au(110) system; their results nicely confirm previous works on C_{60} films [18-20]. In order to allow for a direct comparison between the IPES data (referred to the Fermi level, E_F) and the cross-section curves (referred to the vacuum level, E_v), they have been plotted taking into account the measured work function $e\Phi$ ($e\Phi = E_v - E_F = 4.7 \pm 0.1$ eV, as measured in ref. [21] and [22]). No direct correspondence is found between the maxima in the cross-section curves and the measured unoccupied electronic bands. This rules out the single-particle shape resonance process where the parent state in which the incoming electron gets trapped is the electronic ground state of the neutral molecule [1,2].

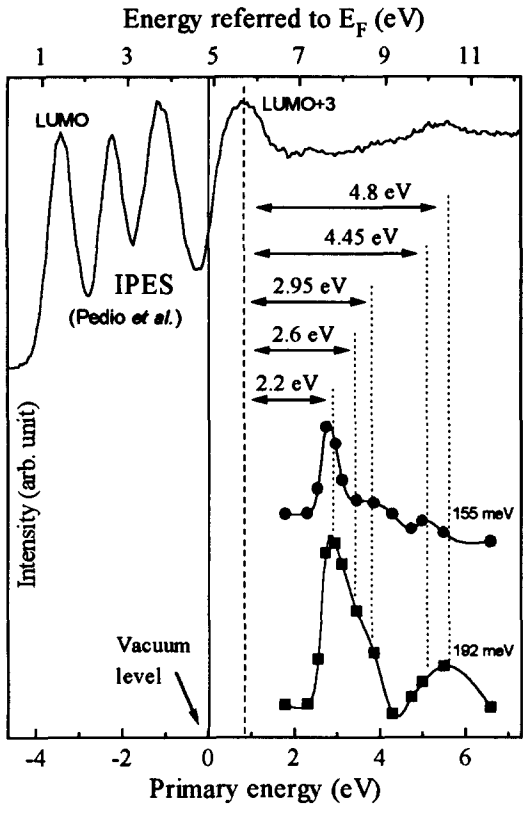

Figure 3: cross-section curves of the 155 meV (circles) and 192 meV (squares) peaks with continuous lines only acting as guides for the eye. The upper curve is an Inverse PhotoEmission spectrum from Pedio *et al.* [17]. The energy separation between the vacuum level and E_F is equal to the work function value.

We should thus turn to an electronic excitation associated resonance [1,2] to explain our results. The parent state for this process is an electronically excited state of the neutral molecule: the incoming electron induces an electronic excitation of the neutral molecule and gets temporarily trapped into a state which matches the residual electron energy. Keeping this process in mind, it is tempting to suppose that the incoming electron is trapped in a LUMO+3 -derived state since LUMO+3 is the first unoccupied orbital above E_v and since it is the last strongly localised orbital, which is an important factor for the interaction with intramolecular vibrational modes.

Looking then at the electronic transition and excitation features observed on thin C_{60} films, one finds out that they could match with the energy separation between LUMO+3 and the cross-section curves at energy positions where one could reasonably assert there is a resonance. The data displayed in Fig. 4 are electronic transitions and excitations measured by Electron Energy Loss Spectroscopy (EELS) from Gensterblum *et al.* [23]. The first main feature of the EEL spectrum is the HOMO-LUMO derived transition appearing at 2.2 eV. This value almost exactly equals the energy separation between the LUMO+3 trapping level and the main resonance feature (around 2.9 eV). The same reasoning holds for the other Π–Π* electronic transitions of the EEL spectrum in the 2 to 5 eV energy range since their energy positions might possibly

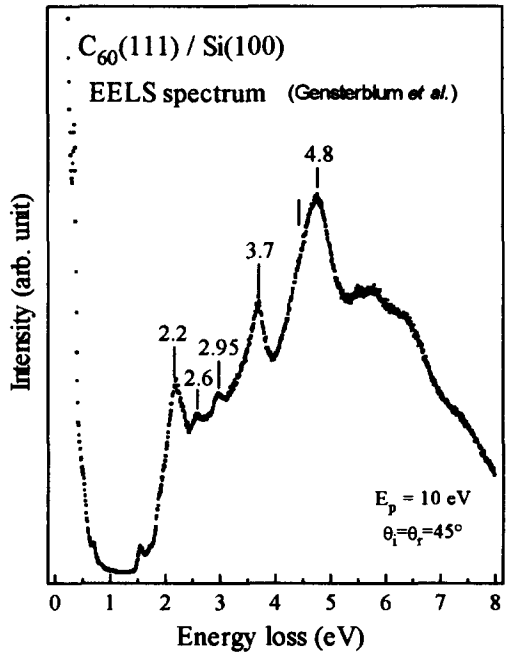

Figure 4: EEL spectrum of a thin C_{60} film with a primary energy of 10 eV [23]. The lowest feature above the band gap (1.55 eV) is of excitonic origin while all structures between 2.2 and 5 eV are Π–Π* interband transitions.

correspond to further resonance features. The cross-section curves for the other vibrational structures which have not been plotted in Fig. 3 all have different shapes but their main features also seem to correlate with Π–Π* electronic transitions. Moreover, the 147, 163 and 178 meV cross-section curves give evidence for a coupling to the 3.7 eV transition that was not observed in the two cross-section curves of Fig. 3.

4. CONCLUSIONS

A resonant behaviour for the vibrational excitation of C_{60} intramolecular vibrations has been identified in this work with a clear peak around 2.9 eV in the cross-section curves. Other features were observed in the cross-section curves but due to the large error bars and the absence of any available theoretical support, their assignment as resonances remains only tentative. Nevertheless, all our results are consistent with an electronic excitation associated resonance process with the incoming electron trapped in the localised LUMO+3 band of the electronically excited host molecule. This resonant interaction with solid C_{60} is a kind of electron attachment which might also account for the very limited inelastic mean free path of low energy electrons in fullerene-based materials [24].

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